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Fluorogenic Polydiacetylene Supramolecules: Immobilization, Micropatterning, and Application to Label-Free Chemosensors

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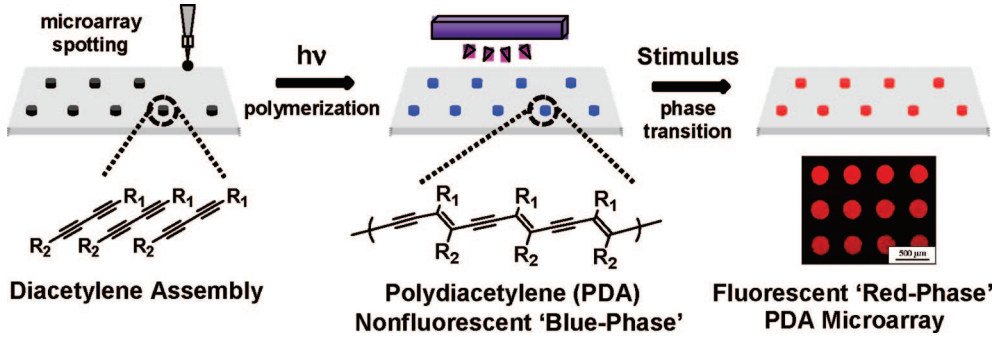
CONSPECTUS



This Account describes a new strategy for the preparation of label-free sensor systems based on the fluorogenic properties of the conjugated polymer, polydiacetylene (PDA). PDA has been extensively investigated as a sensor matrix, owing to a brilliant blue-to-red color transition that takes place in response to environmental perturbations. It has been known for some time that "blue-phase" PDAs are nonfluorescent while their "red-phase" counterparts fluoresce. For the most part, however, the significance of the different fluorogenic properties of PDAs has been ignored in the context of sensor applications. In the course of developing PDA-based sensors, we discovered that PDA vesicles can be readily immobilized on solid substrates. This is an attractive property of PDAs since it leads to the combined advantages of the vesicle sensors (which have three-dimensional interactions between sensor and target molecules) and film sensors (which are applicable to a two-dimensional array or chip format). Stable blue-phase immobilized PDAs can be prepared by employing one of three strategies involving the formation of covalent adducts, biotin–avidin complexes, or complexes formed through nonspecific physical adsorption. A procedure for generating well-patterned fluorescence images is necessary for the immobilized PDAs to function in chip-based sensor systems. Patterned fluorescence images are readily constructed by employing (1) the photolithographic technique, (2) the micromolding in capillaries (MIMIC) method, or (3) an array spotting system. Heat treatment of the patterned "blue-phase" PDA vesicles transforms the nonfluorescent images into their fluorescent red forms. The observation that finely resolved fluorescence patterns can be generated by heat treatment of microarrayed PDAs is highly significant in that it indicates that fluorescence signals might be produced by specific molecular recognition events. Indeed, red fluorescence emission is observed when immobilized PDAs are subjected to specific molecular recognition events, such as ligand−cyclodextrin or protein–protein interactions. The facile immobilization of PDA vesicles on solid substrates and the affinity-induced fluorescence emission combine to make this system applicable to the fabrication of label-free PDA sensors. Since in theory any molecular recognition event that promotes the blue-to-red color transition of PDAs should result in the generation of fluorescence, it should be possible to reformat a variety of previously described colorimetric PDA sensors into fluorescence-based sensor systems. The fluorescence properties of PDAs, when combined with modern methods for the fabrication of microarrays, should stimulate the development of a number of new label-free chemosensor systems.

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